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**Solid-State NMR Characterization of ^{13}C - and ^{15}N -Labelled Phthalimides:
Model Compounds for Studying Polyimides**

WILLIAM L. JARRETT, C. GREG JOHNSON, and LON J. MATHIAS*
University of Southern Mississippi
Department of Polymer Science
Hattiesburg, Mississippi 39406-0076

Abstract

^{15}N CSA spectra were acquired for four isotopically labelled bisphthalimide compounds. The ^{15}N CSA tensor elements (δ_{11} , δ_{22} , and δ_{33}) for the labeled derivatives were determined from CSA lineshape analysis. In addition, the CSA spectrum for the ^{15}N - ^{13}C labelled N-methylphthalimide was obtained. From CSA lineshape analysis it was determined that δ_{33} lies approximately along the N-C bond axis, with δ_{22} assumed to be approximately perpendicular to the imide plane. The angles α and β were found to be 90° and 7° , respectively. The dipolar coupling constant for ^{13}C - ^{15}N bond was 883 Hz, corresponding to a bond length of 1.51 Å.

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WILLIAM L. JARRETT, C. GREG JOHNSON, and LON J. MATHIAS*

University of Southern Mississippi
Department of Polymer Science
Hattiesburg, Mississippi 39406-0076

INTRODUCTION

High-resolution solution and solid-state NMR techniques have been used for a number of years to characterize biological and polymeric systems. Until the last 10-15 years, however, techniques which only observe the isotropic chemical shift (δ_{iso}) value were utilized, thereby ignoring the valuable information that may be obtained from the δ tensor, which is sensitive to the structural and chemical environment of the observed site. Recently, with the advent of isotopic labelling techniques, researchers have been able to determine the principle components of the δ tensor (δ_{11} , δ_{22} , and δ_{33}) for a variety of ^{13}C and ^{15}N labelled organic compounds (1). In addition, the use of dipole-coupled solid-state NMR spectroscopy to determine the orientation of the δ_{33} tensor with respect to the dipolar coupling axis has been used on peptides and polypeptides, (2) nitrosobenzenes, (3) and oximes (4). In some instances the orientation of the δ tensor element with respect to the local molecular structure has been determined (2b-f,3,4). A two-dimensional variation of this technique has been used to study the chain conformation of some oriented proteins (5). Although this particular technique has been used for biological systems, its application to synthetic

polymers has been rare. In addition, little has appeared regarding the magnitude and orientation of δ or for imides, a key component in polyimides a family of generally semi-crystalline, heterocyclic polymers used extensively when excellent physical properties and thermal stability are required.

Tensor evaluations of biological polymers are usually based on labelled model compound studies; thus, a series of labeled model imide compounds based on the phthalimide moiety $(C_6H_4(CO)_2N-R)$ with $R = -H, -CH_3, -C_{18}H_{33}, -CH_2C_6H_5$ have been synthesized and analyzed by solid-state ^{15}N NMR spectroscopy. In addition, $N-[^{13}C]\text{methyl}-[^{15}N]\text{phthalimide}$ was synthesized and its solid-state ^{15}N NMR spectrum acquired in order to obtain information on the orientation of the δ tensor with respect to the local molecular geometry, with the eventual purpose of this study to apply this information to ^{15}N -labelled polyimides.

EXPERIMENTAL

NMR Measurements

CP/MAS spectra: Solid-state CP/MAS NMR spectra were obtained on a Bruker MSL-200 equipped with a Bruker MAS probe operating at 50.32 and 20.287 MHz for ^{13}C and ^{15}N , respectively. Powdered samples were placed in fused zirconia rotors fitted with Kel-F[®] caps and spun with dry air, with rotation rates of 4 to 5 kHz for carbon MAS and 2 to 3 kHz for nitrogen MAS. The ^{13}C spectra were referenced to external adamantane (29.5 ppm), while ^{15}N spectra were referenced downfield from external glycine (0 ppm). The 1H 90° pulse was 4.5 μs

for ^{13}C acquisition and $6.0\ \mu\text{s}$ for ^{15}N acquisition, while a mixing pulse of 2 ms and a 50 ms acquisition period were used in acquiring spectra for each nuclei. A recycle delay of 210 s, corresponding to $\sim 3\text{--}4\ ^1\text{H}\ T_1$ s, was used for observation of both nuclei.

Powder spectra: Solid-state ^{15}N chemical shift anisotropy (CSA) spectra were acquired with the same probe used for CP/MAS work except that the spinning rate was set to zero. For ^{15}N powder spectra, a spin-echo sequence with a tau delay of $200\ \mu\text{s}$ was used to minimize artifacts due to pulse bleed-through. In addition, a 90° flip-back pulse was implemented at the end of acquisition in order to circumvent the long $^1\text{H}\ T_1$ s. The $^1\text{H}\ 90^\circ$ pulse width was $\sim 3.98\text{--}4.05\ \mu\text{s}$, the acquisition time was 50 ms, and the recycle delay was 30 s. The cross-polarization contact time was 5 ms. The number of scans acquired varied from 2560 - 3200, respectively. All chemical shift values are referenced to glycine (0 ppm).

CSA simulations: Chemical shift anisotropy (CSA) spectra were simulated using the POWFIT program developed by Dr. T. G. Oas (6). Fits were done by performing analyses on either the zeroth or first derivative of selected regions of the experimental spectrum. In addition, the theoretical spectrum was convoluted with lorentzian and gaussian line broadening to reproduce the natural line broadening present. All simulations were done on a MicroVax 3100.

Synthesis

All reagents were obtained from Aldrich Chemical Company and used without purification. Dimethylformamide (DMF) was reagent grade and used as received.

A typical procedure for the preparation of an N-substituted phthalimide is as follows: A clean, dry flask was charged with equimolar amounts of [^{15}N] potassium phthalimide and methyl iodide (for the N-methylphthalimide) followed by enough N,N-dimethylformamide (DMF) to give a mixture that was 15 - 20% solids by weight. The flask was submerged in a preheated oil bath at $-60\text{ }^{\circ}\text{C}$ for 2 to 3 hours. The cooled reaction mixture was poured into rapidly stirring water (10 times reaction volume). The precipitate was collected and recrystallized from aqueous ethanol (70 to 85 % yield). For the doubly labelled N-[^{13}C]-methyl-[^{15}N]-phthalimide compound, the above procedure was followed except that ^{13}C labelled methyl iodide was used.

RESULTS AND DISCUSSION

A. ^{15}N -labelled model imides CSA spectra: Figure 1 shows the CSA spectra for the four model imides along with the spectral simulations used to determine the values of δ_{11} , δ_{22} , and δ_{33} ; these values are summarized in Table 1. The calculated spectra fit well to the experimental data, with some variation probably due to anisotropic T_2 and cross-polarization effects.⁶ From Table 1 it is apparent that the major contributor to changes in the δ_{iso} are due to the δ_{22} component. This is consistent with previous work by Shoji and coworkers which

showed that δ_{22} was quite sensitive to molecular composition and conformation (at least in the case of polypeptides) (7).

B. Doubly-labelled N-methylphthalimide: Figure 2 shows the experimental and simulated CSA spectra for ^{15}N - ^{13}C labelled N-methylphthalimide. The CSA spectrum is modulated by both the magnitude of the ^{15}N - ^{13}C dipolar coupling and its orientation with respect to the δ axis system. Table 2 gives the values of δ_{11} , δ_{22} , δ_{33} , α , β , and the ^{15}N - ^{13}C dipolar coupling constant used for the simulation. From the values of α and β the orientation of the N-CH₃ bond vector with respect to the δ axis system was determined; this is shown in Figure 3. Note that the most shielded tensor δ_{33} lies approximately along the N-CH₃ bond. From the magnitude of the ^{15}N - ^{13}C dipolar coupling constant, the length of the ^{15}N - ^{13}C bond is calculated to be 1.51 Å.

C. Discussion: The invariance of the δ_{33} tensor indicates that the N-R σ bond is fairly consistent for the various substituents. Instead, it would appear that the change in substituents mainly effect the π electron density at the nitrogen site. Such an explanation would explain the large variation in the δ_{22} tensor, if it is assumed that this tensor is approximately perpendicular to the imide plane. A computational study investigating the nature of the bonding about the ^{15}N site is currently in progress in order to assign the complete orientation of the δ axis system with respect to the molecular axis system. Such assignments are beyond the scope of the present paper.

SUMMARY

A procedure has been developed for incorporating ^{15}N and ^{13}C isotopic labelling into N-substituted phthalimides, for use as model imides for studying polyimides. From solid-state ^{15}N NMR spectroscopic and computational methods, the values of the δ shift tensor for the model imides were determined. In addition, for N- ^{13}C -methyl- ^{15}N -phthalimide, the δ_{33} tensor was found to lie approximately along the N-CH₃ bond axis, and the N-CH₃ bond length was determined to be 1.51 Å. Future work concerning the determination of the δ tensor orientation with respect to the molecular frame is in progress.

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Table 1. ^{15}N Chemical Shift Data for ^{15}N Labelled Model Imides.^a

Compound	$\delta_{100}^{(\text{exptl})b}$	$\delta_{100}^{(\text{calc})c}$	δ_{11}	δ_{22}	δ_{33}	η^d
Phthalimide	121.5	121	165	136	62	0.492
N-methylphthalimide	119.8	119	177	125	55	0.813
N-stearylphthalimide	128.9	128	172	157	55	0.274
N-benzylphthalimide	134.2	135	179	165	60	0.189

^a All data reported in ppm and referenced to glycine ($\delta_{100}=0.0$ ppm).

^b Based on ^{15}N CP/MAS spectral analysis.

^c Determined by $1/3(\delta_{11} + \delta_{22} + \delta_{33})$.

^d $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{100})$

Table 2. ^{15}N Chemical Shift Parameters for N-[^{13}C]-methyl[^{15}N]-phthalimide.^a

δ_{11}	δ_{22}	δ_{33}	α	β	D
179	125	55	90	7	893

^a All values for the chemical shift tensor are in ppm. The values of α and β are referenced with respect to the N-CH₃ bond axis. The value of the dipolar coupling constant D is in hertz.

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FIG. 1. ^{15}N CSA spectra of a) phthalimide, b) N-methylphthalimide, c) N-stearyl imide, and d) N-benzylphthalimide. All spectra were apodized using a Kaiser digital filter ($\alpha = 4$, $N = 3-5$ ms) and zero-filled to 8092 data points before Fourier transformation. Experimental data is represented by open circles, spectral simulation by a solid line.

FIG. 2. Experimental and simulation ^{15}N CSA spectra of doubly labelled N-methylphthalimide. The experimental data is represented by open circles, the spectral simulation by a solid line. The raw data was processed in the same manner as the spectra in FIG. 1.

FIG. 3. Orientation of the N-CH_3 bond with respect to the δ axis system.

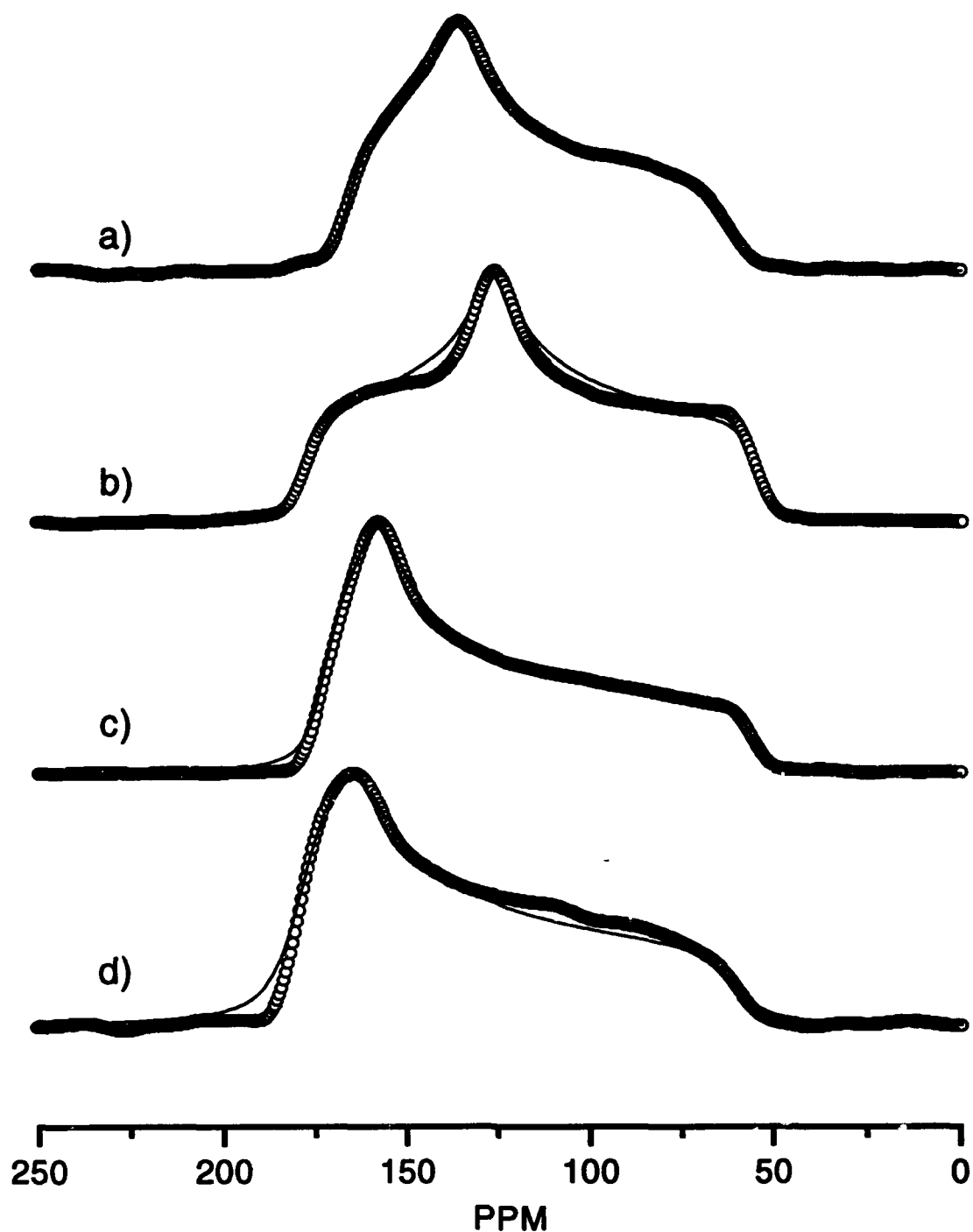


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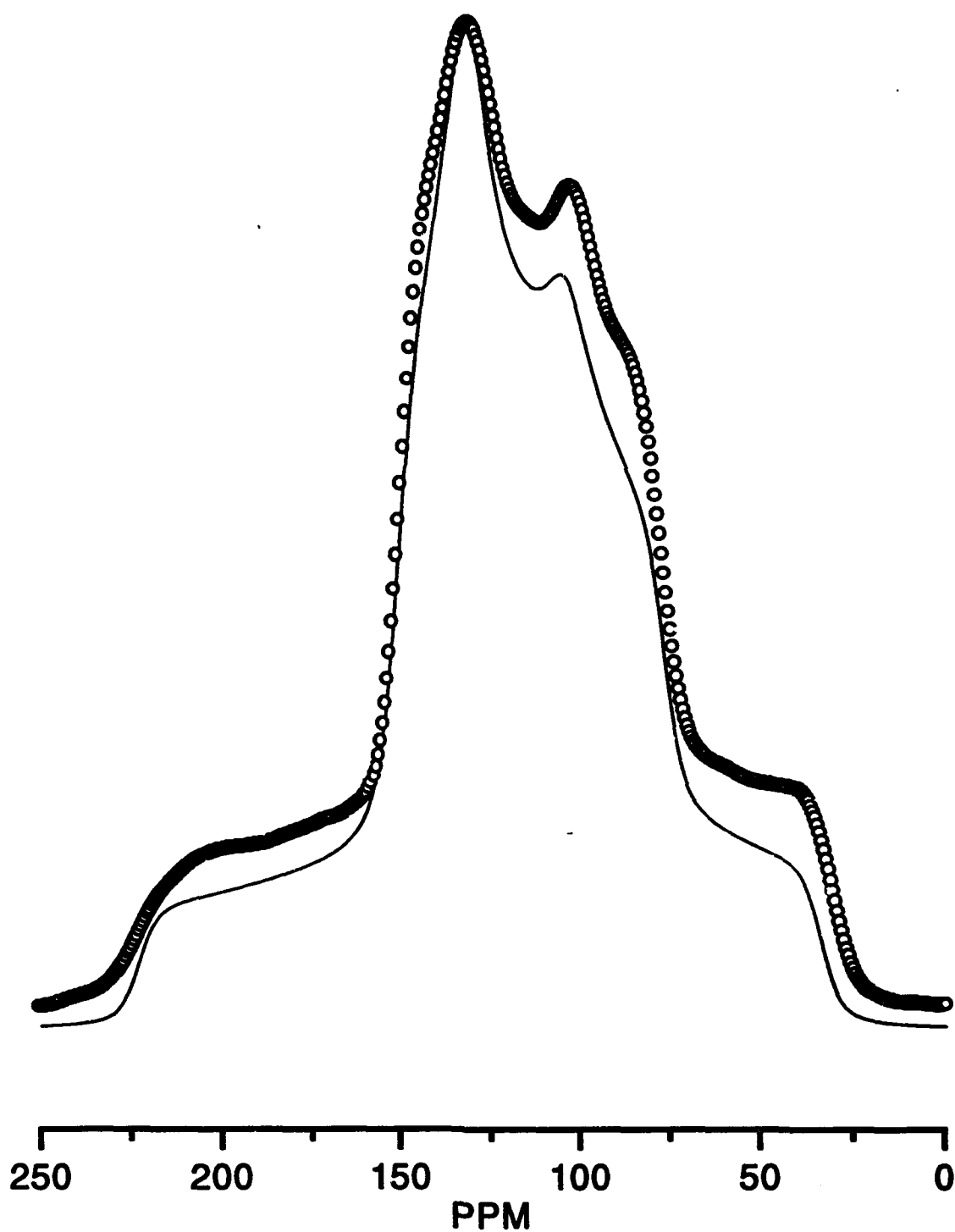


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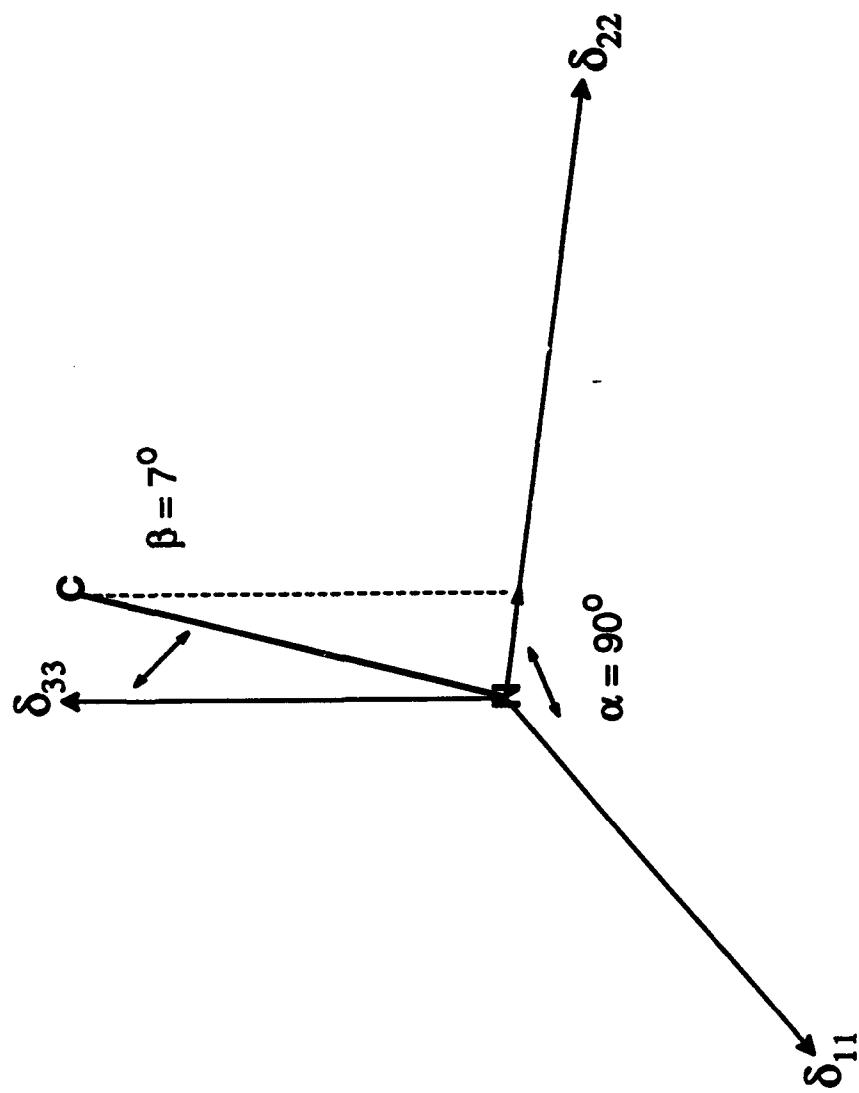


FIG. 3. Orientation of the N-CH₃ bond with respect to the δ axis system.